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(54) A microbiocidal formulation for domestic use

(57) A microbiocidal formulation for prevention, inhibition and removal of microorganisms, especially fungi, living in an indoor environment, which essentially consists of 0.01% - 5% by weight of mixture of a sulphur-containing aromatic compound and a triazine compound dissolved in a solvent. The sulphur-containing aromatic compound may be an isothiazolinone, anilinothiazoline, thiadiazolo-pyrimidine, pyridinethiol-1-oxide, or di-iodomethyl-p-tolylsulfone. The formulation is produced in an easily usable and handleable form and can be employed in aerosols.

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A MICROBIOCIDAL FORMULATION FOR DOMESTIC USE

Field of the invention

The present invention relates to a microbiocidal formulation for domestic use, which hampers the growth of microorganisms inhabiting our daily living environment and causing a lot of problems, kills reproductive microorganisms, and thus solves the problems. Herein, "microorganisms" mean organisms which are invisible to the naked eye and are capable of growing and reproducing by themselves. Their examples include virus, bacteria, yeast, fungi, algae, etc. Among them, fungi mainly is the focus of the present invention, and yet yeast as well as bacteria are not excluded from the invention.

Description of the Prior Art

Microorganisms are very closely associated with our lives and are freely available in the environment. Some of them are helpful and can be beneficial for human being, whereas there are also harmful ones which may cause some problems of causing various diseases in human being, emitting offensive odor, and transforming products which may cause ugly looking. In particular, fungi live in damp undergrounds or closed spaces (wardrobe, footwear room, etc), give off offensive odor, transform products and may cause diseases. Also, they live

in the wallpapers indoors and result in the above-mentioned problems specially in the rainy and humid seasons.

Fungi are the microorganisms having the following characteristics: 1) eucaryotic protists having nuclei in the cells, 2) some of them lead to an independent and self-support life while most of them gather and reproduce to form mycelia and are existed in populations, 3) high reproductivity, 4) rapid growth under the condition of water and proper nutrient, 5) maintenance of their persistent lives by forming spores in environmental conditions unfavorable for other microorganisms, and 6) especially since fungi spores are very light and dry, they can disperse in the air easily, move to other areas and commence new reproduction, and also are inhaled to a person via respiratory tract, and thus cause allergies as well as respiratory ailments. With these characteristics, it has been observed that prevention of reproducing fungi and killing the reproduced fungi are very difficult.

The conventional methods for preventing the reproduction of fungi include a method of placing naphthalene in a closed space, a drying method, a method of using humidity remover, a method of spraying a chlorine-containing microbiocidal formulation, etc. However, these methods generally have their limits. In brief, the method of placing naphthalene must be placed only in a closed space and accompanies offensive odor; the drying method requires continuous use and

thus provide inconvenience for domestic use. Also, its effect is lukewarm at the underground regions surrounded by high humidity and in the rainy seasons. The humidity remover is restricted in places and dosage ranges and takes considerable effective time. The chlorine method does not maintain microbiocidal effect for long time since water used as a solvent provides humidity and rather helps the reproduction of fungi.

SUMMARY OF THE INVENTION

Accordingly, an object of the invention is to overcome the above-identified drawbacks of conventional methods and thus solves the problems caused by microorganisms (especially, fungi) living in our environment.

In order to achieve the object, the present invention provides a microbiocidal formulation produced by selecting a microbicide which is nearly non-toxic to human body, can prevent the reproduction of fungi as well as yeast, and can kill the reproductive organisms, dissolving the microbicide in a nearly non-toxic solvent, and filling the mixture in aerosol or spray container, and its use.

The microbiocidal formulation of the present invention can be employed in the prevention and removal of fungi growing in the wall, ceiling, floor covered with laminated paper,

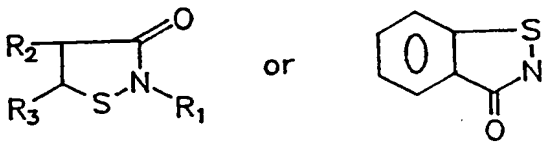
wardrobes and footwear room, sterilization of air conditioner filter, and removal of fungi living in the car and underground and their offensive odor. That is, the present formulation can be widely used in solving the problems caused by microorganisms living in our environment.

As a microbicide of the present invention, all of compounds known to have microbiocidal activity against the above-mentioned microorganisms can be employed. Among them, sulphur-containing aromatic compounds as well as triazine compounds are more preferable because these compounds are nearly non-toxic to human body and have a wide range of microbiocidal activity spectrum. In addition, as a solvent, alcohols having hydroxy group of 1 to 10 carbon atoms, water, or their mixture are useful since they can dissolve the active compounds well, are nearly non-toxic to human body, and have advantageous microbiocidal activity.

Examples of sulphur-containing aromatic compounds as a microbiocidal ingredient (hereinafter referred to active ingredient) include isothiazoline derivatives of general formula (I), anilinothiazoline derivatives of general formula (II), thiadiazolo pyrimidine derivatives of general formula (III), pyridinethiol-1-oxide compounds of structural formula (IV) and diiodomethyl-p-tolylsulfone compounds of structural formula (V), etc. In addition, example of triazine compounds include triazine triethanol compound of general

formula (VI), etc.

It has been found that isothiazolinone derivatives have microbiocidal activity against bacteria and fungi and are used as a microbicide for the farming and gardening (see; Korean Patent Publication No. 70-140 and 88-1349 and Japanese Patent Publication No. 7999/1983).



(I)

wherein, R_1 represents C_{1-18} alkyl group, C_{3-5} cycloalkylhalogen lower alkyl group, or C_{1-10} lower alkoxy substituted alkyl group, aryl group, halogen, nitro group, lower alkyl group, lower alkylacylamino lower carboalkoxy or sulphamyl substituted aryl lower hydroxyalkyl group, lower haloalkyl group, lower dialkylaminoalkyl group or carbamoyl group of -C-NHR';

R_2 and R_3 are hydrogen, halogen or selected from lower alkyl group when R_1 is methyl or ethyl except that both of R_2 and R_3 are hydrogen and R_1 is carbamoyl group;

R_2 represents hydrogen, lower alkyl group, halogen, or cyano when R_1 is carbamoyl and also R_2 is hydrogen, halogen,

lower alkyl group, or lower haloalkyl when R_3 is hydrogen, lower alkyl group or halogen;

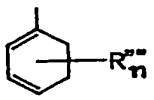
R_3 represents, lower alkylthio lower alkylsulphynyl group, or lower alkylsulphonyl when R_2 is cyano;

X represents oxygen or sulphur; and

R' represents C_{1-18} alkyl group, lower alkylsulphonyl group, anilsulphonyl group, halogen or lower alkyl substituted anilsulphonyl group or carboalkoxyalkyl of R"-OC-R"'

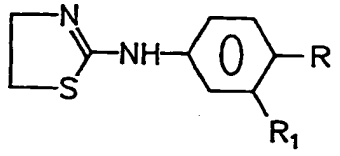
O

wherein, R" represents lower alkyl group and R"' Represents C_{1-4} alkylene group or alkyl group of



(wherein, R"" is lower alkyl group, halogen, nitro group or C_{1-4} alkoxy group, n is integral number of 0-3).

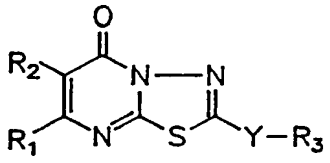
It has been found that anilinothiazolidine compounds of general formula (II) have antifungal activity and are used as an ingredient for pharmaceuticals (see; Korean Laid-open Patent Publication No. 88-9950).



(II)

wherein, R represents C_{4-8} alkyl group and one of R_1 and R is hydrogen and R_1 is C_{5-8} straight chained alkyl group.

It has been also found that triazolopyrimidine compounds of general formula (III) have physiologically active properties and are used as a microbicide for the farming and gardening (see; Korean Patent Publication No. 90-7545 and 90-7546).



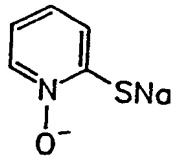
(III)

wherein, R_1 represents alkyl group or aryl group;

R_2 represents hydrogen, halogen, nitro group, carboalkoxy group or alkyl group; and

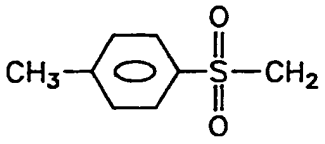
R_3 represents alkyl group or aralkyl group and Y represents -SO- or $-SO_2-$.

It has been found that pyridinethiol-1-oxide of structural formula (IV) has microbiocidal activity against fungi.



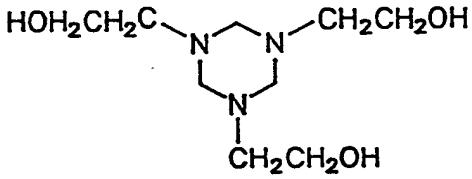
(IV)

It has been found that diiodomethyl-p-tolyl sulfone has microbiocidal activity against fungi.



(V)

It has been found that triazine triethanol compound of structural formula (IV) is used as a remover of cutting oil in the industrial field.



(VI)

The above-described active ingredients have been widely used for the farming and gardening, pharmaceuticals or industrial field. However, their another new use for removing harmful microorganisms living in indoor environment is not known to the public.

Therefore, an object of the present invention is to provide a microbiocidal formulation for domestic use which can eliminate the microorganisms living in indoor environment with known active compounds, is nearly non-toxic for human body, and is convenient for use. The present formulation is produced according to the following steps; selecting sulphur-containing aromatic compound or the mixture of sulphur-

containing aromatic compound and triazine compounds mixed in proper amounts, as an active ingredient, dissolving the active ingredient in a non-toxic alcohol solvent having microbiocidal activity, and thus providing a microbiocidal formulation in the form of aerosol for convenient use. Preferable amount range of an active ingredient in a solvent is between 0.01% and 5.0% by weight.

The following data from the Acute Toxicity Test demonstrates that the present formulation comprising 0.01% - 5.0% of active ingredient by weight in the solvent is non-toxic to human body. This test was carried out according to the Toxicity Test standards of Pharmaceuticals established by the Korean National Health & Safety Institute, 1988 and the Method described in Casarette & Doll, Texioology, 4th ED:

Triazine triethanol: LD_{50}(acute skin toxicity)-4,760mg/kg rat

Isothiazolinone compounds: LD_{50}(acute skin toxicity)-3,600mg/kg rat

Diiodomethyl-p-tolylsulphone: LD_{50}(acute skin toxicity)-200,000mg/kg rat

Pyridinethiol-1-oxide: LD_{50}(acute oral toxicity)-2,800mg/kg rat

The following examples are provided in embodiments for the present invention and should not be constructed as limiting. In the examples, percentages are by weight.

Example 1: Collection of Microorganisms and Test of Microbiocidal Activity

About 100 representative species from microorganisms living in the walls, floors covered with laminated paper, and ceilings in general houses, and decorations or ornaments in underground stores were collected. Isolation was carried out by the following steps; isolating a part living in microorganisms with a flame-sterilized platinum loop slightly, moving the said part to a growth medium prepared sterilly in vitro, incubating for 3 days at 25°C, and isolating 16 species microorganisms having different characteristics from the medium on the basis of shape, color and size. Examples of 16 species are Aspergillus sp., Penicillium sp., Cladosporium sp., Rhizopus sp., Trichoderma sp., Alternaria sp., Chactomium sp., Stachybotrys sp., Aureobasidium sp., Nigrospora sp., Emerioella sp., Rhodotorula sp., Scopulariopsis sp., Ulooladium sp., Saccharomyces sp., and Candida sp..

The ingredients of the medium used in the isolation were depicted in the following Table 1.

Table 1

Malt Extract	40 g
Peptone	10 g
Agar	15 g
Chloramphenicol	10 mg
Distilled Water	1 l

In order to select an effective microbiocidal material, compounds known as having microbiocidal activity were tested.

The test is summarized as follows:

16 species of microorganisms grown in the medium of Table 1 were treated with 12 species of compounds at constant concentration and after 24 hours, growth degree of each of the microorganisms was compared.

As can be seen from the following Table 2, among 12 species, sulphur-containing aromatic compounds such as isothiazolinone derivative, anilinothiazoline derivatives, thiadiazolopyridine derivatives, pyridinethiol-1-oxides, diiodomethyl-p-tolylsulfone, and triazine triethanol compounds were appeared to have the strongest microbiocidal activity.

Table 2

micro-biocide	concentration	solvent	#1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Siccanin	0.2%	D.W.	++	++	++	++	+	++	++	++	++	++	++	++	++	++	++	++
Miconazole	0.2%	D.W.	++	++	++	++	+	-	++	++	++	+	+	+	++	+	+	+
T.C.H.	0.3%	D.W.	-	—	-	-	-	—	+	-	-	—	+	+	++	+	-	-
Catechol	0.2%	D.W.	++	++	++	++	++	++	++	++	++	++	++	++	++	++	++	++
Benzoate	0.4%	D.W.	++	++	++	++	++	++	++	++	++	++	++	++	++	++	++	++
T.T.	0.15%	D.W.	—	—	—	—	+	—	+	—	—	—	+	—	—	—	+	-
I.T.Z.	0.15%	50%EtOH	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
A.T.	0.3%	95%EtOH	—	—	—	—	—	—	—	-	—	—	—	—	—	-	-	-
P.T.O.	0.1%	95%EtOH	—	-	—	—	—	—	-	—	—	—	—	—	—	—	—	—
D.T.S.	0.05%	95%EtOH	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
T.P.	0.3%	95%EtOH	—	—	-	-	-	-	-	—	-	-	—	—	+	-	-	-
EtOH	95%	95%EtOH	++	++	++	++	++	++	++	++	++	++	++	++	++	++	++	++

abbreviations and symbols denote:

T.C.H. (Tincture of Cortex Hibisoi)

T.T. (Triazine Triethanol)

I.T.Z. (Isothiazolinone)

A.T. (Anilinothiazoline)

T.P. (Thiadiazolo pyrimidine)

P.T.O. (pyridinethiol-1-oxide)

D.T.S. (Diiodomethyl-p-tolylsulfone)

EtOH(Ethyl Alcohol)

++: grow well

+: grow but slowly

-: not grow well

--: no growth

*: the number of microorganism collected.

Example 2 : Solvent Test

This example discloses the relationship of microbiocidal activity and solvent for dissolving active ingredients. Test was carried out as follows: 4 representative species of microorganisms such as Aspergillus sp., Penicillium sp., Cladosporium sp., and Alternaria sp., were selected from the isolated microorganisms; active ingredients were added to kinds of solvents as depicted in Table 3; the mixtures were sprinkled over media inoculates with the above microorganisms to make their surface wet; and then microorganism groups as

controls which ware non-treated with microbicide and the microorganism groups which were subjected to microbicide treatment were together incubated for 3 days at 25°C, and degree of growth was compared.

For solvent test, solvents which can dissolve active ingredients well were primarily chosen, among tested solvents, and the active ingredients in solvent were investigated whether maintaining the microbiocidal activity. In conclusion, solvents which can dissolve the active ingredients well had no effect on microbiocidal activity. And then, solvents which are non-toxic to human, less-odor and volatile were chosen for the practical use of the present invention. In consideration of this, it is understood that among tested solvents, C_{1-10} alcohols having at least one hydroxy are preferable and the smaller is the number of carbon, the better is the result.

Also, it is possible to use the mixture of alcohols and water according to practical purposes, because this mixture also keeps its microbiocidal activity and the mixture of water, and other organic solvents besides alcohols can be used and they also have no effect on microbiocidal activity.

Table 3

solvent	Biocide	Solubility	* #1			#8			#10			#13		
			Co	Mx	Tr	Co	Mx	Tr	Co	Mx	Tr	Co	Mx	Tr
methyl alcohol	P.T.O.	OO	++	—	—	++	—	—	++	—	—	++	—	—
ethyl alcohol	D.T.S	OO	++	—	—	++	—	—	++	—	—	++	—	—
propyl alcohol	T.P.	OO	++	—	—	++	—	—	++	—	—	++	—	—
isopropyl alcohol	A.T.	O	++	—	—	++	—	—	++	—	—	++	—	—
butyl alcohol	I.T.Z.	O	++	—	—	++	—	—	++	—	—	++	—	—
pentyl alcohol	T.T.	O	++	—	—	++	—	—	++	—	—	++	-	—
hexyl alcohol	D.T.S	O	++	—	—	++	-	—	++	—	—	++	-	—
acetone	P.T.O.	O	++	—	—	++	-	-	++	-	-	++	-	-
ethyl acetate	I.T.Z.	O	++	—	—	++	-	—	++	-	—	++	-	—
diethyl acetate	T.T.	X	/	/	/	/	/	/	/	/	/	/	/	/
n-pentane	P.T.O.	XX	/	/	/	/	/	/	/	/	/	/	/	/
n-hexane	A.T.	XX	/	/	/	/	/	/	/	/	/	/	/	/

abbreviations and symbols denote:

OO: Degree of solubility is very good

O: Degree of solubility is good

X: Degree of solubility is bad

XX: Degree of solubility is zero

++: grow well

-: not grow well

--: no growth

/: no test

*: the number of microorganism

Co: control, no treatment

Mx: addition of active ingredient to the mixture of water and organic solvent

Tr: addition of active ingredient to the organic solvent

T.T.: Triazine Triethanol

I.T.Z.: Isothiazolinone

A.T.: Anilinothiazoline

T.P.: Thiadiazolo Pyrimidine

P.T.O.: Pyridinethiol-1-oxide

D.T.S.: Diiodomethyl-p-tolylsulfone

Example 3 : Investigation of Microbiocidal Activity at Respective Combinations and Concentrations of Active Ingredients

Microbiocidal activity was investigated at respective

combinations and concentrations of 6 species of excellent active compounds selected from Example 1.

The above 6 active compounds in respective combinations and concentrations were added to growth media in Table 1 as depicted in Table 4. Thereafter, 4 representative species taken from isolated microorganisms were inoculated and incubated for 3 days at 25°C, and degree of growth was observed. It revealed selected 6 species of active compounds showed excellent microbiocidal activity at the concentration of 0.01%-5% and also, use of combinations of the compounds exhibited similar effect.

Table 4

No.	active ingredient/ concentration	microbiocidal activity (Degree of growth) #1	8	10	13
1	T.T.(0.01%)	++	++	++	++
2	T.T.(0.1%)	+	+	++	++
3	T.T.(1%)	—	—	—	-
4	T.T.(5%)	—	—	—	—
5	I.T.Z.(0.01%)	-	-	-	+
6	I.T.Z.(0.1%)	—	—	—	-
7	I.T.Z.(1%)	—	—	—	—
8	I.T.Z.(5%)	—	—	—	—
9	A.T.(0.01%)	+	++	++	++
10	A.T.(0.1%)	-	+	-	+
11	A.T.(1%)	—	-	—	-
12	A.T.(5%)	—	—	—	—
13	P.T.O.(0.01%)	+	-	+	++
14	P.T.O.(0.1%)	—	—	—	—
15	P.T.O.(1%)	—	—	—	—
16	P.T.O.(5%)	—	—	—	—
17	D.T.S.(0.01%)	-	-	-	-
18	D.T.S.(0.1%)	—	—	—	—
19	D.T.S.(1%)	—	—	—	—
20	T.P.(0.01%)	+	+	++	++
21	T.P.(0.1%)	-	-	-	-
22	T.P.(1%)	—	-	—	—
23	T.P.(5%)	—	—	—	—
24	I.T.Z.(0.1%)+T.T.(1%)	—	—	—	—
25	A.T.(1%)+T.T.(1%)	—	—	—	—
26	P.T.O.(0.1%)+T.T.(1%)	—	—	—	—
27	D.T.S.(0.1%)+T.T.(1%)	—	—	—	—
28	T.P.(1%)+T.T.(1%)	—	—	—	—

abbreviations and symbols denote:

T.T.: Triazine Triethanol

I.T.Z.: Isothiazolinone

A.T.: Anilinothiazoline

T.P.: Thiadiazolo Pyrimidine

P.T.O.: Pyridinethiol-1-oxide

D.T.S.: Diiodomethyl-p-tolylsulfone

++: grow well

+: grow but slowly

-: not grow well

--: no growth

*: the number of microorganism

Example 4 : Comparative Experiment of Microbiocidal Activity Between Naphthalene and Humid Remover

Using microorganisms in Examples 3, comparative experiment of the microbiocidal activity between naphthalene and humid removers was accomplished. These materials are known as having advantageous activity against reproduction of fungi. In order to increase antifungal activity against fungi, 40g of naphthalene containing p-dichlorobenzene was employed and 300g of humid remover was used. First, fungi were liquid-cultured with the medium in Table 1 excluding agar and then the culture in suitable amounts were scattered to a closed space of 1 m^2. The solid medium in Table 1 was

laid in a closed space and maintained under the condition of 25°C and over 80% of humidity.

After this, 4 conditions were made;

1) No addition of any components in a closed space (described in Table 5 as Cont)

2) Addition of naphthalene in a closed space (described in Table 5 as Naph)

3) Addition of humidity remover in a closed space (described in Table 5 as H.P.)

4) Addition of D.O. of the invention in a closed space (described in Table 5 as D.O.)

(D.O. means 300ppm of D.T.S. (Diiodomethyl-p-tolylsulphone dissolved in 95% ethylalcohol and 20ml of D.O. was daily scattered at one time for 3 days)

Each of medium was left in open state for 24 hours and then incubated in closed state for next 4 days at 25°C. Finally, the number of colonies appeared at the surface of medium was counted and microbiocidal activity was compared.

Results are presented in Table 5

Table 5

(unit: Colony/Plate)

day/condition	cont	Naph	H.P.	D.O.
1st day	350	330	360	160
2nd day	330	190	260	65
3rd day	400	150	250	60
4th day	250	130	200	31
5th day	210	110	190	25

abbreviations and symbols denote:

cont, Naph., H.P., D.O., are previously mentioned

As can be seen from the above Table 5, respective numbers of microorganisms treated with Naph., H.P., and D.O. are smaller than those of control. Also, it was noted that the superiority of microbiocidal activity of D.O. was about 4 times that of Naph and about 7.5 times that of H.P..

Example 5: Comparative Experiment of Microbiocidal Activity Between The Present Formulation and ClO_2 Containing Product

Using the 4 representative species of microorganisms in example 3, the comparative experiment of microbiocidal activity between the present formulation and ClO_2-containing product was carried out. The reason why ClO_2 was chosen as

a comparative object was that this compound is used as a main component of disinfectant, sterilizing agent, odor removal agent which are commercially available.

The above 4 species of microorganisms were incubated in growth media for 3 days at 25°C and cultured to form a colonies having 1 cm of diameter on central region of Petri dish. And then, 5 conditions were made as depicted in Table 6; each of control (no treatment), ethyl alcohol treated only (Et), 0.1% of active ingredient in ethyl alcohol (1X), 1.0% of active ingredient in ethyl alcohol (10X) and ClO_2-containing commercial product (Ci) was scattered to make the surface of the media wet sufficiently. At this time as an active ingredient, pyridinethiol-1-oxide and triazine triethanol in Table 2 were employed in volume ratio of 2:8. After scattering, media were left for 10 minutes and further left for 5 days at 25°C. As a result, the reproduction of microorganisms was inhibited for at least 3 days in case of the present mixture-treated media, whereas the reproduction of microorganisms was stimulated in case of ClO_2-containing product since water included in product and air produced on scattering blow fungi's spores to another area and rather help their reproduction. This result demonstrates that the present formulations are superior in microbiocidal activity to ClO_2-containing microbiocidal formulations.

Table 6

condition	* #1					#8					#10					#13				
day	Co	Et	1X	10X	Cl	Co	Et	1X	10X	Cl	Co	Et	1X	10X	Cl	Co	Et	1X	10X	Cl
1st day	+	-	—	—	+	+	-	—	—	+	+	-	—	—	+	+	-	—	—	+
2nd day	+	+	—	—	++	+	+	—	—	++	+	+	—	—	++	+	+	-	—	++
3rd day	++	+	—	—	++	++	++	-	—	++	++	+	—	—	++	++	++	-	—	++
4th day	++	++	-	—	++	++	++	-	—	++	++	++	-	—	++	++	++	+	—	++
5th day	++	++	-	—	++	++	++	+	—	++	++	++	-	—	++	++	++	+	-	++

abbreviations and symbols denotes:

Co (Control), Et, 1X, 10X, Cl were explained in the above.

++; grow with wide spread

+; grow with spread

-; grow with slight spread

--; grow without spread

Example 6 : Experiments of Utility of Aerosol or Spray Form

This example discloses the comparison between scattering of a microbicide comprising active ingredient dissolved in solvent in the form of aerosol or spray pulverizer and direct application of a microbicide in liquid by use of brush. In both cases, there was no difference in microbiocidal activity. However, direct application had advantage in handling narrow areas with high concentration and but had difficulties in handling lofty region beyond person's reach or wide area and producing inconvenience on use. On the contrary, the scattering method by aerosol or spray pulverizer overcame the above identified difficulties and thus provided a convenient and simple usage; could be used in the lofty region or narrow space; and could handle the wide area equally within a short time. Because of these advantages, the present invention shows that use of the formulation in the form of aerosol or

spray is more effective for practical purposes and also on use with water as in cases of microbicide for humidifier or cleaner. It is more effective to use in liquid form.

Example 7 : Field Test

This example describes that the field test with microbiocidal formulation containing 300ppm of diiodomethyl-p-tolylsulfone as an active ingredient dissolved in ethyl alcohol and minute amounts of spices was carried out. This test focused its object on microorganisms living in the walls of general houses and the walls and tree ornaments of underground stores.

Field test is summarized as follows;

Inoculating the above-identified microorganisms on growth medium by use of a sterilized platinum loop;

Scattering the microbicide to make the surface of medium wet sufficiently by spray pulverizer filled with freon gas. Microbicide was scattered for 3 days at one time daily after scattering, leaving the medium for 1-2 days;

Inoculating the microorganisms on another medium by means of a sterilized platinum loop; and

Incubating this medium for 3 days at 25°C.

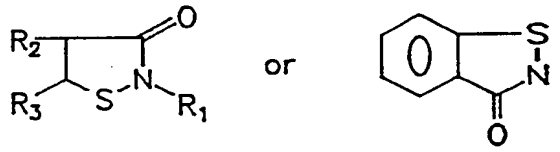
After 3 days, the result of comparing the growth of microorganisms before and after treatment of microbicide was that all of the microorganisms in the growth medium inoculated

before treatment with microbicide were grown, whereas all of the microorganisms in the growth medium inoculated after treatment with microbicide were not grown at general houses and under ground stores, From this, it is understood that the present formulation can inhibit the growth of microorganisms effectively in the field with less amounts than in the laboratory.

WHAT IS CLAIMED IS:

1. A microbiocidal formulation for prevention, inhibition and removal of microorganisms, especially fungi, living in indoor environment, which essentially consists of 0.01%-5% by weight of mixture of a sulphur-containing aromatic compound and a triazine compound dissolved in solvent.

2. A formulation according to claim 1, wherein the said sulphur-containing aromatic compound comprises an isothiazolinone derivative of general formula (I), an anilinothiazoline derivative of general formula (II), a thiadiazolo pyrimidine derivative of general formula (III), a pyridinethiol-1-oxide compound of structural formula (IV) and a di-iodomethyl-p-tolylsulfone compound of structural formula (V).



(I)

wherein, R_1 represents C_{1-18} alkyl group, C_{3-6} cycloalkylhalogen lower alkyl group, or C_{1-10} lower alkoxy substituted alkyl group, aryl group, halogen, nitro group, lower alkyl group, lower alkylacylamino lower carboalkoxy or

sulphamyl substituted aryl lower hydroxyalkyl group, lower haloalkyl group, lower dialkylaminoalkyl group or carbamoyl group of -C-NHR';

R_2 and R_3 are hydrogen, halogen or selected from lower alkyl group when R_1 is methyl or ethyl except that both of R_2 and R_3 are hydrogen and R_1 is carbamoyl group;

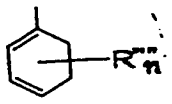
R_2 represents hydrogen, lower alkyl group, halogen, or cyano when R_1 is carbamoyl and also R_2 is hydrogen, halogen, lower alkyl group, or lower haloalkyl when R_3 is hydrogen, lower alkyl group or halogen;

R_3 represents, lower alkylthio lower alkylsulphonyl group, or lower alkylsulphonyl when R_2 is cyano;

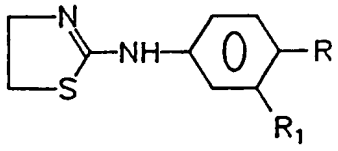
X represents oxygen or sulphur; and

R' represents C_{1-18} alkyl group, lower alkylsulphonyl group, anilsulphonyl group, halogen or lower alkyl substituted anilsulphonyl group or carboalkoxyalkyl of R"-OC-R"'

wherein, R" represents lower alkyl group and R"' Represents C_{1-4} alkylene group or alkyl group of

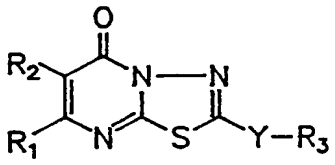


(wherein, R"" is lower alkyl group, halogen, nitro group or C_{1-4} alkoxy group, n is integral number of 0-3);



(II)

wherein, R represents C_{4-8} alkyl group and one of R_1 and R is hydrogen, or R is hydrogen and R_1 is C_{5-8} straight chained alkyl group;

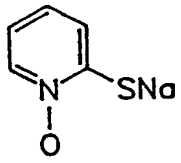


(III)

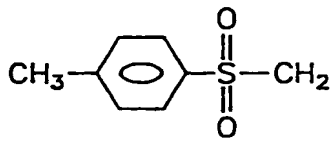
wherein, R_1 represents alkyl group or aryl group;

R_2 represents hydrogen, halogen, nitro group, carboalkoxy group or alkyl group; and

R_3 represents alkyl group or aralkyl group and Y represents -SO- or $-SO_2-$;

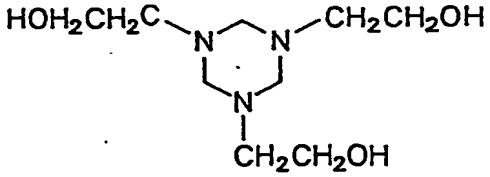


(IV)



(V)

3. A formulation according to claim 1, wherein said triazine compound comprises a triazine triethanol compound of general formula (VI).



(VI)

4. A formulation according to claim 1, wherein said solvent comprises one selected from a group consisting of an alcohol having at least one hydroxy group of 1 to 10 carbon atoms, a water, and a mixture thereof.

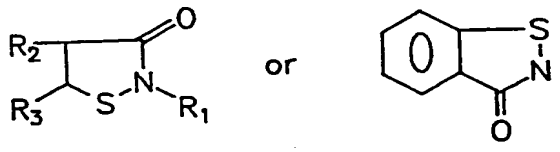
5. A microbiocidal Product produced for the removals of fungi living in the walls, floors covered with laminated paper, wardrobes footwear rooms, etc of general houses, the sterilizations of a drain, a garbage can, a bathtub, a washstand, an humidifier, and an air conditioner filter, and the removals of fungi living in a car and a underground store,

and offensive odor therefrom, which comprises a formulation according to any one of claims 1-4.

6. A microbiocidal product produced in aerosol form filled with freon gas or LPG, spray pulverizer form, and concentrated liquid form attenuatable from concentrated formulation on use, which comprises a microbiocidal formulation according to any one of claims 1-4.

7. A microbiocidal formulation for prevention, inhibition and removal of reproduction of microorganisms, especially fungi, living in our surroundings, which comprises 0.01%-5% by wight of a sulphur-containing aromatic compound dissolved in a solvent.

8. A formulation according to claim 7, wherein said sulphur-containing aromatic compound comprises an isothiazolinone derivative of general formula (I), an anilinothiazoline derivative of general formula (II), a thiadiazolo pyrimidine derivative of general formula (III), a pyridinethiol-1-oxide compound of structural formula (IV) and a di-iodomethyl-p-tolylsulfone compound of structural formula (V).



(I)

wherein, R_1 represents C_{1-18} alkyl group, C_{3-6} cycloalkylhalogen lower alkyl group, or C_{1-10} lower alkoxy substituted alkyl group, aryl group, halogen, nitro group, lower alkyl group, lower alkylacylamino lower carboalkoxy or sulphamyl substituted aryl lower hydroxyalkyl group, lower haloalkyl group, lower dialkylaminoalkyl group or carbamoyl group of $-\overset{\overset{X}{\|}}{C}-NHR'$;

R_2 and R_3 are hydrogen, halogen or selected from lower alkyl group when R_1 is methyl or ethyl except that both of R_2 and R_3 are hydrogen and R_1 is carbamoyl group;

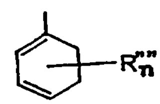
R_2 represents hydrogen, lower alkyl group, halogen, or cyano when R_1 is carbamoyl and also R_2 is hydrogen, halogen, lower alkyl group, or lower haloalkyl when R_3 is hydrogen, lower alkyl group or halogen;

R_3 represents, lower alkylthio lower alkylsulphonyl group, or lower alkylsulphonyl when R_2 is cyano;

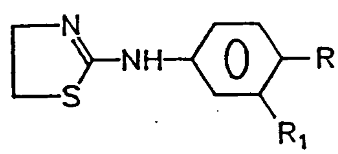
X represents oxygen or sulphur; and

R' represents C_{1-18} alkyl group, lower alkylsulphonyl group, anilsulphonyl group, halogen or lower alkyl substituted anilsulphonyl group or carboalkoxyalkyl of $R''\text{-O}\underset{\underset{O}{\|}}{C}\text{-}R'''$

wherein, R" represents lower alkyl group and R"' Represents C_{1-4} alkylene group or alkyl group of

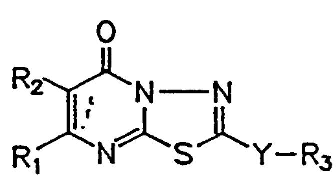


(wherein, R"" is lower alkyl group, halogen, nitro group or C_{1-4} alkoxy group, n is integral number of 0-3);



(II)

wherein, R represents C_{4-8} alkyl group and one of R_1 and R is hydrogen, or R is hydrogen and R_1 is C_{5-8} straight chained alkyl group;

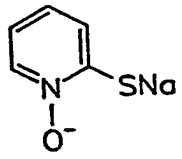


(III)

wherein, R_1 represents alkyl group or aryl group;

R_2 represents hydrogen, halogen, nitro group, carboalkoxy group or alkyl group; and

R_3 represents alkyl group or aralkyl group and Y represents -SO- or $-SO_2-$;



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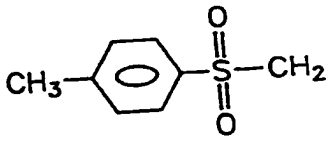
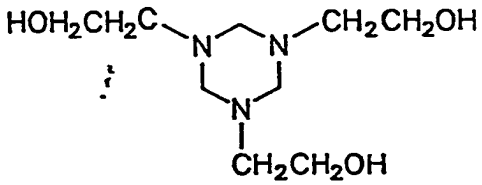


(V)

9. A formulation according to claim 7, wherein said triazine compound comprises a triazine triethanol compound of general formula (VI).



(VI)

10. A formulation according to claim 7, wherein said solvent comprises one selected from a group consisting of an alcohol having at least one hydroxy group of 1 to 10 carbon atoms, a water, and a mixture thereof.

11. A microbiocidal Product produced for the removals of fungi living in the walls, floors covered with laminated paper, wardrobes footwear rooms, etc of general houses, the sterilizations of a drain, a garbage can, a bathtub, a washstand, an humidifier, and an air conditioner filter, and the removals of fungi living in a car and a underground store, and offensive odor therefrom, which comprises a formulation according to any one of claims 7-10.

12. A microbiocidal product produced in aerosol form filled with freon gas or LPG, spray pulverizer form, and concentrated liquid form attenuatable from concentrated formulation on use, which comprises a microbiocidal formulation according to any one of claims 7-10.

Patents Act 1977 Exami 's report to the Comptroller under Section 17 The Search report)	Application number GB 9302486.7
Relevant Technical Fields (i) UK Cl (Ed.M) A5E (EBB, ES) (ii) Int Cl (Ed.5) A01N 43/66	Search Examiner P N DAVEY Date of completion of Search 2 MARCH 1994
Databases (see below) (i) UK Patent Office collections of GB, EP, WO and US patent specifications. (ii) ONLINE DATABASES: WPI	Documents considered relevant following a search in respect of Claims :- 1-6

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A:	Document indicating technological background and/or state of the art.	&:	Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
X	GB 2088718 A (CIBA-GEIGY) See eg Example 1	1

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